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INTRAMOLECULAR FLEXIBILITY OF RELATIVELY RIGID POLYMERS, AND IN--ETC(U)
JAN 81 D BHAUMIK, W J WELSH, J E MARK AFOSR-78-3683
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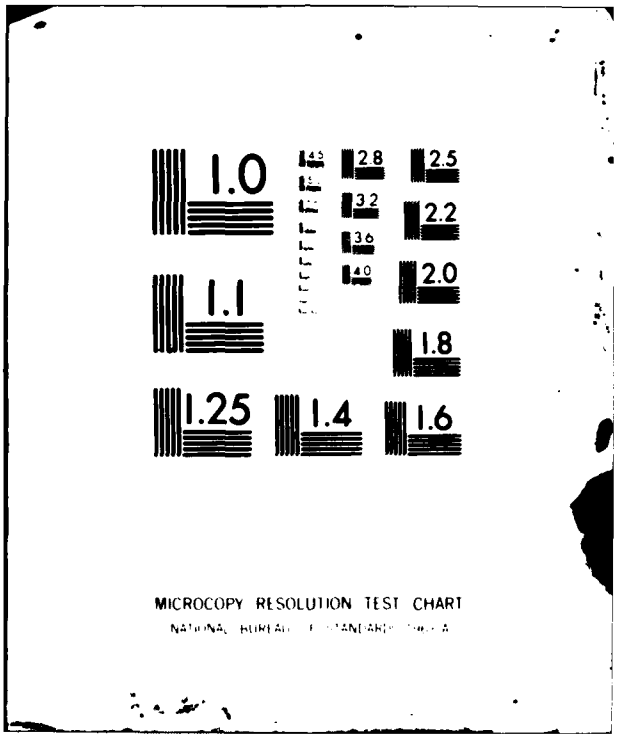
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Conformational energy calculations were carried out on benzoxazole and benzothiazole polymers in order to determine whether or not the molecules are planar and if not, the extent of their nonplanarity. Such information is highly relevant to the nature of the chain packing in the crystalline and liquid-crystalline states. Intermolecular interactions were also investigated, both with regard to their effect on the extent to which the chains approach the desired coplanar conformations.

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Block 20: Abstract (continued)

and with regard to the origin of the high mechanical strengths of these materials and their resistance to almost all common solvents. The polarizabilities of these molecules were also estimated using a variety of theoretical methods; this information should be very useful in the interpretation of solution property studies, such as flow birefringence measurements used to obtain rheological information relevant to the processing of these materials. A series of wholly aromatic heterocyclic swivels were also characterized with regard to their flexibilities in both the unprotonated state and in the protonated state present in the strongly acidic media used as solvents for these polymers.

INTRAMOLECULAR FLEXIBILITY OF RELATIVELY RIGID POLYMERS, AND INTERMOLECULAR INTERACTIONS IN ORDERED POLYMER SYSTEMS, PART II

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Air Force Office of Scientific Research

January, 1981

FOREWORD

This report was prepared at the Department of Chemistry of the University of Cincinnati, under Grant AFOSR-78-3683. The research described was administered under the direction of the Air Force Office of Scientific Research, Bolling Air Force Base, Washington, D.C. 20332.

The report covers work carried out between October 1, 1979, and September 30, 1980, and was prepared in January, 1981.

RESEARCH OBJECTIVES

The purpose of the present investigation is to use semi-empirical and quantum-mechanical methods to obtain information on the physical properties of rigid-rod benzoxazole and benzothiazole polymers which are of importance to the Air Force because of their high mechanical strength and excellent thermal stability. Such calculations involve energy calculations on both intramolecular (conformational) effects and interchain interactions. Of particular interest is the extent to which the various ring structures in the chains deviate from coplanarity, and how these deviations affect the ordering of the chains in the crystalline and liquid-crystalline states. A second area of importance is the nature and magnitudes of the interchain interactions, for both the protonated and unprotonated chains. Also of great interest are the effects of oxygen, sulfur, and wholly aromatic "swivels" on the processability of these materials, the ordering of the chains, and the mechanical strenth of the resulting films or fibers. The basic goals are thus a molecular understanding of the unusually high strengths of these materials, and knowledge regarding how currently available structures could be modified to improve these strengths. Also to be obtained is sufficient information on intermolecular interactions to provide guidance on improving processability by modification of the structure and rigidity of the chains, or by incorporation of a suitably chosen diluent or plasticizer. Polarizability calculations are carried out in support of various experimental studies of the polymers in solution, and

calculations relevant to other aspects of electronic structure are explored with regard to types of conductivity which may be of interest for electronic applications of these materials.

Some theoretical and experimental investigations are also carried out on more tractable random-coil polymers such as the polyoxides, polyformals, and polysulfides in order to obtain more insight into the properties of the structurally related rigid-rod polymers.

STATUS OF THE RESEARCH EFFORT

Planarity, or departures therefrom, can be of considerable importance in the formation of either crystalline or liquid-crystalline phases in rigid-rod polymeric systems. Four aromatic-heterocyclic polymers, *cis* and *trans* polybenzoxazoles (PBO) and polybenzothiazoles (PBT), form such phases, and energy calculations were therefore carried out to characterize any deviations from planarity arising from *p*-phenylene group rotations along these chain backbones. Intramolecular (conformational) energy calculations indicate that the two PBO polymers should be planar, and this conclusion is in agreement with experimental results obtained on pertinent model compounds. Similar calculations on the PBT polymers correctly predict nonplanarity, but overestimate its magnitude. Inclusion of intermolecular contributions (chain-packing effects) in this case considerably improves the agreement between theory and experiment.

Interaction energies between the relatively rigid PBO and PBT polymers were also calculated, in an attempt to gain insight into the very high mechanical strength and unusual solvent resistance of these materials. The predicted details of the chain packing and the corresponding densities were found to be in good agreement with experimental results obtained on relevant model compounds in the crystalline state. The interaction energies are estimated to be very large, with van der Waals contributions being far more important than Coulombic ones. Additional calculations indicate that protonation of the chains should greatly decrease the intermolecular attractions, even at very high dielectric constant. This conclusion is consistent with the fact that only extraordinarily strong acids are solvents for these types of chain molecules.

Three theoretical methods were used to calculate the polarizabilities of the repeat units of two PBO's and one PBT. Second-order perturbation theory coupled with a CNDO method gave average polarizabilities that were unrealistically small. More reliable results were obtained from two empirical methods, one based on the additivity of atomic hybrid components of the polarizability, and the other on the additivity of bond polarizabilities. The results of these two approaches were in good agreement with one another, and the latter gave a value of the anisotropic ratio which is in at least qualitative agreement with an experimental value calculated in the very rough approximation that the chains are cylindrically symmetrical.

Another theoretical investigation employed the CNDO/2 method

with direct geometry optimization to calculate the intramolecular conformational energies for the wholly aromatic swivels biphenyl, 2,2'-bipyridyl, 2-phenylpyridine, 2,2'-bipyrimidyl, and 2-phenylpyrimidine, in order to assess their flexibility. The species mono- and di-protonated 2,2'bipyridyl, 2,2'-bipyridyl-H_3O^+, and 2,2'-bipyrimidyl-$2H_2O$ are also investigated in this regard to determine the effects of both acid and aqueous environments on the conformational characteristics of the swivels. In addition, other relevant conformation-dependent properties, such as dipole moments, partial-charge distributions and the calculated optimized geometries were calculated and compared with available experimental data and with the results of other theoretical investigations.

The first of a series of studies of random-coil chain molecules related to the rigid-rod polymers involved poly(1,3-dioxolane). This polymer is generally prepared in a ring-opening polymerization and can thus in principle have structural irregularities from the presence of the two repeat units $CH_2O(CH_2)_2O$ and $(CH_2)_2OCH_2O$. Rotational isomeric state calculations indicate that such irregularities should have a much greater effect on the dipole moments of these chains than they have on their unperturbed dimension, optical anisotropies, and molar Kerr constants.

In a related theoretical study, semi-empirical potential energy functions were used to calculate conformational energies of several alkylene sulfide polymers of structure $[S(CH_2)_y]$. The polymers chosen were those for which crystalline state configurations were known, specifically those having $y = 1$, 2, 3, and 5, respectively. The configurations of minimum conformational

energy were generally found to correspond to the crystalline state configurations. The only exceptions occurred for conformational energy differences close to zero, which is to be expected since in these cases even small differences in intermolecular packing energies could obviously play an important role. Some preliminary comments are also made on the heretofore unstudied polysulfides corresponding to y=4, 6, and higher. Comparisons with the corresponding polyoxides $[O(CH_2)_y]$ help elucidate the effect of the size of the hetero-atom X (S or O), its effective charge, the C-X bond length, and the C-X-C bond angle. The most important difference between the polysulfides and polyoxides appears to be the fact that the C-S bond is considerably longer than the C-O bond.

Semi-empirical potential energy functions were also used to characterize interchain interactions in poly(ethylene sulfide) (PES) $[CH_2CH_2S]$ and in poly(ethylene oxide)(PEO)$[CH_2CH_2O]$, the primary purpose being to elucidate the very high melting point of PES (216°C) relative to that of PEO (68°C). In the case of the PEO chain, the partial charges on the atoms could be calculated by the CNDO/2 method. The charges thus obtained showed only a slight dependence on conformation, thus supporting the assumption of conformation-independent charges usually made in conformational analyses. They were also in good agreement with charges previously estimated from bond dipole moments. The total interchain interactions, significantly attractive in both polymers, were much larger in PES than in PEO, which is consistent with the interpretation of its unusually high melting point in terms

of its enthalpy of fusion. The difference in intermolecular attractions is primarily due to van der Waals interactions, rather than to Coulombic (dipolar) effects. They are traceable to the fact that the S atom has twice as many electrons as the O atom, and thus has a much higher polarizability. The stronger van der Waals attractions in PES are partly due to differences in crystalline-state conformations, in that the S atoms in the PES (2/0) glide-plane conformation are much more exposed than the O atoms in the PEO (7/2) helix. Very approximate estimates of the crystalline state densities of the two polymers were found to be in satisfactory agreement with experiment.

A final, experimental study focused on several semi-organic polymers of unusually good thermal stability. Specifically, the materials were three aryloxyphosphazene copolymers [P(OR)(OR')-N-] with side groups R corresponding to phenyl, and R' to p-ethyl-phenyl, 2,4-dichlorophenyl, and 2-naphthyl, respectively. Each of these polymers was separated into four fractions using fractional precipitations from tetrahydrofuran (THF) solutions, with n-pentane as non-solvent. Two fractions from each were characterized using osmometry and viscometry, in THF at 25°C, thereby providing values of the number-average molecular weight, second virial coefficient, and intrinsic viscosity. This information was used to obtain values of the characteristic ratio $\langle r^2 \rangle_o / nl^2$ of the unperturbed dimensions relative to the number of skeletal bonds and the square of their length. The values of this ratio show a remarkably large dependence on the nature of the side groups, in agreement with the results of two previous investi-

gations. The observed large variations could be due to experimental difficulties known to plague attempts to characterize the solution properties of this class of polymers. If real, however, the differences could be due to the fact that when the two bond angles of the repeat unit of these chains are significantly different, then the most likely regular conformations of these chains correspond to extremely different spatial extensions. Markedly different values of the unperturbed dimensions could thus conceivably result from changes in conformational population arising from relatively small changes in intramolecular interactions, stereochemical composition, chemical composition, or chemical sequence distribution.

CUMULATIVE LIST OF PUBLICATIONS

1. The Flexibility of Various Molecular Swivels Used to Control the Rigidity and Tractability of Aromatic Heterocyclic Polymers, W. J. Welsh, D. Bhaumik, and J. E. Mark, J. Macromol. Sci. - Phys., 18, 000 (1981).

2. Phenylene Group Rotations and Nonplanar Conformations in Some Cis and Trans Polybenzoxazoles and Polybenzothiazoles, W. J. Welsh, D. Bhaumik, and J. E. Mark, Macromolecules, 14, 000 (1981).

3. Interchain Interactions in Some Benzoxazole and Benzothiazole Rigid-Rod Polymers, D. Bhaumik, W. J. Welsh, H. H. Jaffé, and J. E. Mark, Macromolecules, 14, 000 (1981).

4. Polarizabilities of Some Benzoxazole and Benzothiazole Rigid-Rod Polymers, D. Bhaumik, H. H. Jaffe', and J. E. Mark, Macromolecules, 14, 000 (1981).

5. The Flexibility of Biphenyl and Related Species Utilizable As Molecular Swivels in Rodlike Polymers. A CNDO/2 Analysis, W. J. Welsh, H. H. Jaffe', J. E. Mark, and N. Kondo, to be submitted to J. Phys. Chem.

6. Calculations of Molecular Polarizabilities of Some Aliphatic and Aromatic Molecules, D. Bhaumik, H. H. Jaffe', and J. E. Mark, to be submitted to Theoret. Chim. Acta.

7. Random-Coil Configurations of the Polyformals $[CH_2O(CH_2)_yO]$. V. Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants, E. Riande, E. Saiz, and J. E. Mark, Macromolecules, 13, 448 (1980).

8. Crystalline State Configurations of Alkylene Sulfide Polymers, W. J. Welsh, J. E. Mark, and E. Riande, Polymer J., 12, 467 (1980).

9. Calculated Intermolecular Energies Relevant to the Unusually High Melting Point of Poly(Ethylene Sulfide), D. Bhaumik and J. E. Mark, Macromolecules, 14, 000 (1981).

10. Unperturbed Dimensions of Some Aryloxy Polyphosphazenes, A. L. Andrady and J. E. Mark, Eur. Polym. J., 17, 000 (1981).

11. Random-Coil Configurations of the Polyformals $[CH_2\text{-}O\text{-}(CH_2)_y\text{-}O\text{-}]$ VI. Dipole Moments of the Stereochemically Variable Polymer

Prepared from 4-Methyl-1,3-dioxolane, E. Riande, M. Garcia, and J. E. Mark, to be submitted to J. Polym. Sci., Polym. Phys. Ed.

12. Random Coil Configurations of the Polysulfides. I. Dipole Moments of Poly(pentamethylene sulfide), E. Riande, W. J. Welsh, and J. E. Mark, to be submitted to Polymer.

13. Random Coil Configurations of the Polysulfides. II. Dipole Moments of Poly(trimethylene sulfide), W. J. Welsh, J. E. Mark, and E. Riande, to be submitted to Polymer.

14. Random Coil Configurations of the Polysulfides. III. Dipole Moments of Poly(1,3-dithiocane), E. Riande, W. J. Welsh, and J. E. Mark, to be submitted to Polymer.

Preprints and reprints of all papers are sent to the Air Force Office of Scientific Research as they become available. Preprints of the papers dealing directly with the rigid-rod polymers are also sent to all investigators in the Air Force Ordered Polymers Program.

PROFESSIONAL PERSONNEL

1. Dr. J. E. Mark, Senior Investigator; Professor of Chemistry and Director of the Polymer Research Center, The University of Cincinnati.

2. Dr. W. J. Welsh, Postdoctoral Fellow and Adjunct Professor, The University of Cincinnati, and Assistant Professor,

College of Mount St. Joseph.

3. Dr. D. Bhaumik, Postdoctoral Fellow, The University of Cincinnati.

4. Dr. H. H. Jaffé, Professor of Chemistry, The University of Cincinnati.

INTERACTIONS

1. Some of the above material has been presented as part of a general lecture on "Statistical Properties of Chain Molecules" at the University of Minnesota, Bell Telephone Laboratories, The University of Cincinnati, Istanbul Technical University, and the Weizmann Institute of Science.

2. Paper #8 (see preceding Section) was presented at a meeting of the International Union of Pure and Applied Chemistry, Florence, Italy, September, 1980.

3. Papers #1-4 will be presented at a National Meeting of the American Chemical Society to be held in Atlanta in March, 1981.

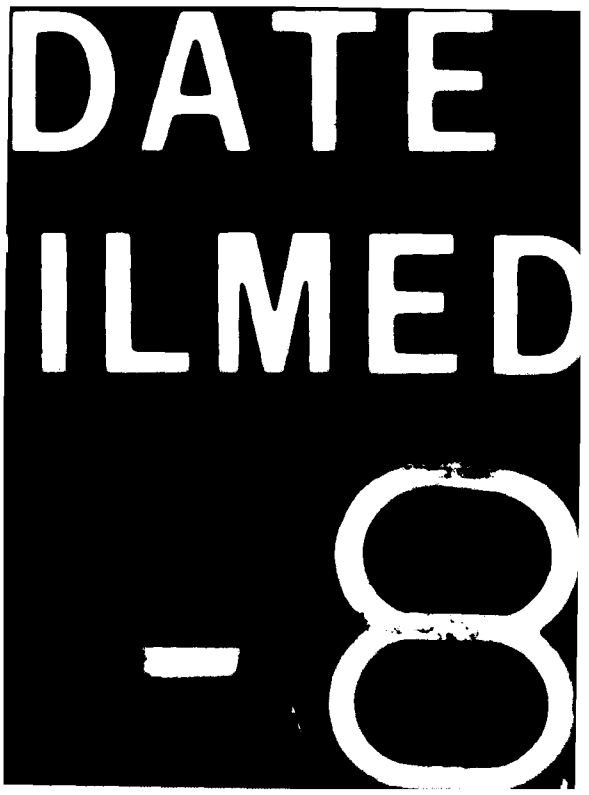
4. Papers #5 and 10 will be presented at a National Meeting of the American Physical Society to be held in Phoenix in March, 1981.

5. Essentially all of the work on the rigid-rod polymers has been presented and discussed in detail at various Reviews

of the Air Force Ordered Polymers Program, organized by Dr. T. E. Helminiak and held approximately semi-annually at the Wright-Patterson Air Force Base in Ohio.

J. E. Mark

January 26, 1981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